

The University of Chicago

THE AUGER EFFECT IN GERMANIUM

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

1937

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MICHAEL FERENCE, JR.

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The Auger Effect in Germanium

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Auger electrons ejected from the L and M levels of germanium are studied by means of a magnetic spectrograph in which the ordinary photographic plate is replaced by a small Geiger-Müller electron counter. The maximum energy of the Auger electrons arising from the $K-L^2$ transition is found to be 8590 ± 15 volts. The kinetic energies of ejected Auger electrons are computed from theoretical considerations and shown to agree well with

those observed. An attempt is made to separate the band of electrons from the L shell into three groups and compare their intensities with theory, but is not entirely reliable because of too low resolving power of the spectrograph. A reliable estimate of the relative probability of transitions $K \rightarrow L^2$ and $K \rightarrow LM$ is made and found to be 100 : 31, which is to be compared with 100 : 58 calculated from the theory.

INTRODUCTION

IT has been known for some time that an atom ionized in the K shell may, on reorganization to the normal state, either emit fluorescence radiation or eject an Auger electron of definite energy.^{1,2} Robinson and Cassie³ in their determination of x-ray levels from electron spectra

measured the energies of a number of these "fluorescence" or Auger electrons. They found the energies to be considerably lower than would be expected for electrons extracted from normal atoms. These investigators, however, made no particular attempt to study the structure of the Auger lines. This paper is a report on some studies of the Auger electrons ejected from germanium; the electrons were recorded by a Geiger-Müller ion counter of the design described by Van den Akker and Watson.⁴

¹ P. Auger, *Comptes rendus* **180**, 65 (1925); *J. de phys. et rad.* **6**, 205 (1926); *Ann. de physique*, Paris **6**, 183 (1926); *Comptes rendus* **182**, 773; 1215 (1926).

² M. de Broglie and J. Thibaud, *Comptes rendus* **180**, 179 (1925).

³ H. Robinson and Cassie, *Proc. Roy. Soc. A* **113**, 282 (1928).

⁴ Van den Akker and Watson, *Phys. Rev.* **31**, 1631 (1931).

APPARATUS

In Fig. 1 is shown the horizontal section through the slits of the magnetic spectrograph used in this research. The spectrograph together with the solenoid for deflecting the photoelectrons is the one designed by Kretschmar⁵ for his precision determination of e/m . The only modification made in the present work was the introduction of the Geiger-Müller tube in place of a photographic plate.

The defining slit S_1 , through which the electrons passed, was 0.2 mm wide. The lead shield P served to keep any scattered x-rays from affecting the counter, while the aluminum baffles A prevented scattered electrons from entering the counter. The heavy lead well L absorbed the main x-ray beam after it had passed through the thin film F of germanium deposited on a strip of Cellophane. The entrance window to the counter W was a disk with a set of 14 holes, each 0.25 mm in diameter and arranged in a vertical line. A thin film of celluloid about 10^{-6} cm thick covered the holes of the small disk. It was necessary that this film be as thin as possible and still strong enough to withstand a difference in pressure of about 6 cm of mercury. A detailed description of the specialized form of Geiger tube used in this research and of its operation is given by Van den Akker.⁶ The tube itself was earthed, while the anode was connected to a source of high potential.⁷ The amplifying circuit was that described by Locher,⁸ modified slightly by the introduction of a power tube between the thyratrons and the Cenco impulse counter.

The electron spectra studied in this paper were obtained when the primary x-rays of silver passing through a palladium filter were allowed to strike a barely visible film of germanium. One can obtain an indication of the amount of germanium on this Cellophane strip from the way in which the metal was deposited. A sheet of Cellophane 10 cm square was folded in two and placed about 20 cm above a tungsten coil containing the germanium. The direct beam of

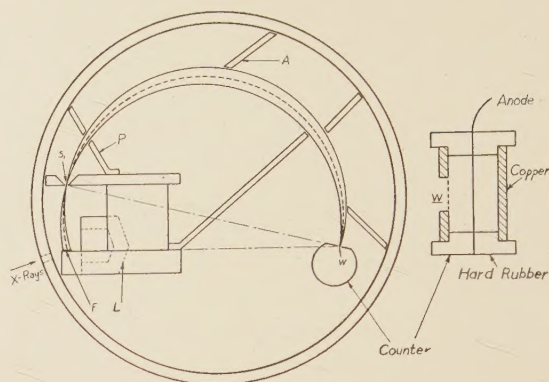


FIG. 1. Diagram of spectrograph with counter.

germanium was deposited on the bottom layer of Cellophane which was discarded. The top layer containing only the trace of germanium that had diffused around the Cellophane sheet was used in this experiment.

The x-rays were produced by a shielded filament, metal x-ray tube operated at 48 kilovolts and 20 milliamperes. By carefully aligning and adjusting the target of the x-ray tube it was possible to obtain counts as high as 320 per minute.

EXPERIMENTAL PROCEDURE

The final data represented by the curves of Fig. 2 were obtained in the following manner. After the apparatus had reached temperature equilibrium, the magnetic field was adjusted for a point on the low velocity side of the L^2 curve and two-minute readings taken for every five milliamperes increment in the field current until a point on the high velocity end of the LM curve was reached. This was repeated, starting, however, from a high velocity point of the LM curve. Each point thus represents the average of two trials. The vertical lines to the left of the L^2 curve show the deviation from the mean of the two sets of readings. The crosses below the L^2 curve represent counts obtained under approximately the same operating conditions as those on the curve except that the germanium film was replaced by a blank Cellophane strip.

In order to plot the readings on a linear volt scale as is done in Fig. 2, it is necessary to calibrate the spectrometer. This was done by calculating the energy of the $AgK\alpha_1 \rightarrow K(Ge)$ photo-

⁵ G. G. Kretschmar, Phys. Rev. **43**, 417 (1933).

⁶ Van den Akker, Rev. Sci. Inst. **1**, 672 (1930).

⁷ T. H. Johnson and J. C. Street, J. Frank. Inst. **214**, 155 (1932).

⁸ G. L. Locher, J. Frank. Inst. **216**, 553 (1933).

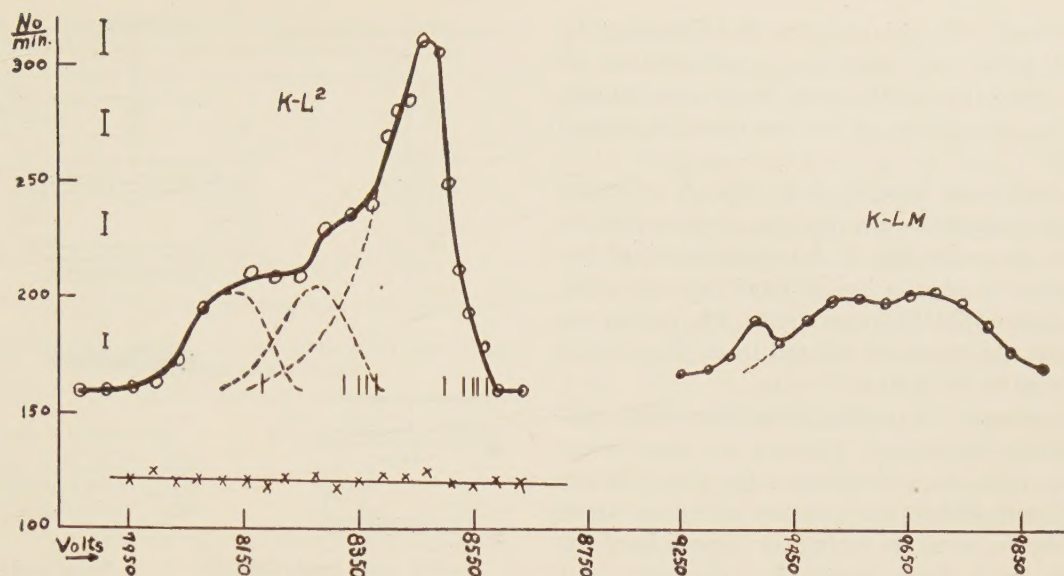


FIG. 2. Showing the Auger electrons due to the $K-L^2$ and $K-LM$ transitions. The vertical lines under the curve represent the position of the electrons of various kinetic energies as calculated from theory.

electrons with the following atomic constants. (Fig. 3.)

$$\begin{aligned} e/m &= 1.769 \times 10^{17} \text{ e.m.u./g} \\ h &= 6.545 \times 10^{-27} \text{ erg sec.} \\ c &= 3 \times 10^{10} \text{ cm/sec.} \\ e &= 4.774 \times 10^{-10} \text{ e.s.u.} \\ R &= 109737 \text{ cm}^{-1}. \end{aligned}$$

These are the same constants that were used by Robinson and Cassie.³ The term values of germanium listed in Table I are taken directly from Siegbahn's book.⁹ The constant of the solenoid, 11,434 oersteds per ampere, was that determined by Kretschmar.⁵

DISCUSSION OF RESULTS

To facilitate the discussion of the results and the interpretation of the above curves recourse will be had to the purely qualitative x-ray energy diagram shown in Fig. 4. The L^2 levels (designated here as Auger levels) arise from the configurations

$$1s^2 \left\{ \begin{array}{l} 2s^0 2p^6 \\ 2s^1 2p^5 \\ 2s^2 2p^4 \end{array} \right\} 3s^2 3p^6 3d^{10} 4s^2 4p^2,$$

while the very large number of LM levels arise

⁹ Siegbahn, *Spektroskopie der Röntgenstrahlen* (Julius Springer, 1931).

from the many configurations possible when an L and M electron are missing.

When an atom is ionized in the K shell, it may find itself in the state $1sK$ with a definite probability proportional to the fourth power of the atomic number¹⁰ for a radiative transition to the $L_{II}L_{III}$ levels, giving rise to the $K\alpha_{12}$ lines of germanium. On the other hand because of the coupling between the discrete level $1sK$ and the continuum of the same energy, say $1s^2 2s^0 Es$

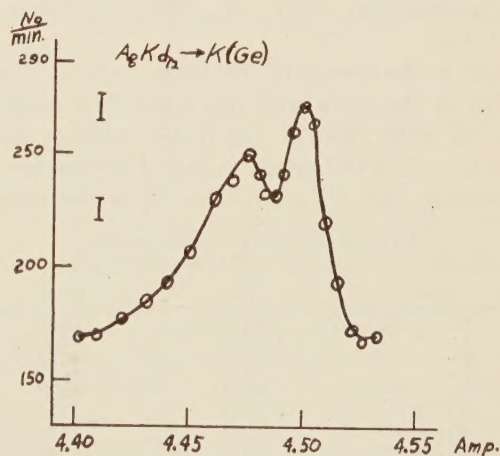


FIG. 3. Showing the two peaks of the K photoelectrons of germanium due to the silver $K\alpha_{12}$

¹⁰ G. Wentzel, *Zeits. f. Physik* 43, 524 (1927).

where $E = K - L^2$, there is a probability that the ionized atom will undergo a radiationless or Auger transition to the level in the continuum, with the expulsion of an electron of energy $K - L^2$.

The electrons arising from the $K - L^2$ and $K - LM$ transitions are the ones represented by the two curves of Fig. 2. A measurement of the high velocity edge of the L^2 band thus fixes the lower limit of the L^2 Auger levels. The maximum energy of the electrons ejected from these levels was found to be 8590 ± 15 volts.

Any attempt to predict from theoretical considerations the kinetic energies of Auger electrons involves the estimation of the energy levels of an atom which has lost two electrons from inner shells. Accurate estimates of such levels in sodium have been made by Kennard and Ramberg¹¹ because of the connection of these levels with the satellites of the x-ray diagram lines. Because of the low resolving power of the β -ray spectrograph used in the present work, an estimate of the accuracy of that of Kennard and Ramberg seems unnecessary, and a comparatively rough method, with the use of Slater's¹² system of screening constants, has been used. By this means the *excess* energy required to remove an L electron when one L electron is already missing has been obtained. In Table II are summarized the numerical details of the calculation of the energy of the normal germanium atom. Table III gives the energies of the germanium atom in different states of excitation.

If E_1 is the energy of the normal atom, E_2 the energy of the atom with one L electron missing, and E_3 with two L electrons missing, then $E_L = E_1 - E_2$ is the energy required to remove one L electron and $E_{L'} = E_1 - E_3 - E_L$ is the energy

TABLE I. Germanium term values.

TERM	v/R	VOLTS
K	817.6	11066
L_1	103.9	1406
L_{11}	91.6	1240
L_{111}	89.3	1209
M_I	12.9	175
$M_{II, III}$	8.8	119
$M_{IV, V}$	1.8	24

¹¹ Kennard and Ramberg, Phys. Rev. **46**, 1034, 1040 (1934).

¹² J. C. Slater, Phys. Rev. **36**, 57 (1930).

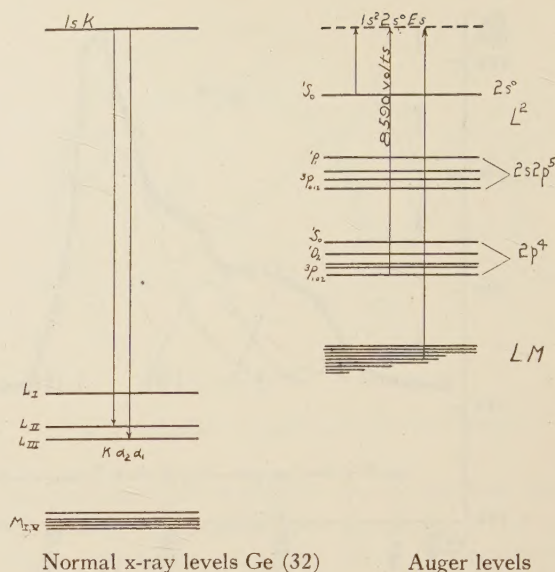


FIG. 4. Some of the more important Auger levels in germanium.

required to remove the second L electron. The *excess* energy, therefore, required to pull out an L electron when one L electron is already missing is $(E_{L'} - E_L) = 2E_2 - E_1 - E_3 = 5.3$ Rydberg units or 72 volts. From the empirical x-ray data of Table I, one finds the energy of the lowest L^2 level to be $2(1209) + 72 = 2490$ volts, and the maximum energy of the electrons, given by $K - L^2$, to be $11066 - 2490 = 8576$ volts. The agreement with the observed value is satisfactory.

If we confine our attention to the levels arising from a doubly ionized L shell, their locations and relative energies can be predicted with some confidence. From ordinary spectroscopic theory, the following J values (total angular momenta) are known to arise from a doubly ionized L shell.

Configuration	J 's
$2s^0 2p^6$	0
$2s^1 2p^5$	0, 1, 1, 2
$2s^2 2p^4$	0, 0, 1, 2, 2

The relative spacings of these levels will depend on the coupling, or ratio of the exchange energy to the spin-orbit energy in the various configurations.

It is convenient to locate the levels which would arise from extreme jj coupling, and then to discuss the deviations from these hypothetical

TABLE II. Showing the details of the calculation of the energy in Rydberg units of the normal germanium atom.

ELECTRON SHELLS	Z_{eff}	$\left(\frac{Z_{\text{eff}}}{n}\right)^2$
$1s^2$	31.70	2009.8
$2s^2 2p^6$	27.85	1551.3
$3s^2 3p^6$	20.85	382.7
$3d^{10}$	10.85	130.8
$4s^2 4p^2$	5.65	9.3
$E_1 = \sum_i (Z_{\text{eff}}/n_i)^2 = -4083.9$		

TABLE III. The energies of the germanium atom under various states of excitation.

ELECTRON CONFIGURATIONS	ENERGIES IN RYDBERG UNITS	DESIGNATION
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$	-4083.9	E_1
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$	-3985.1	E_2
$1s^2 2s^2 2p^4 3s^2 3p^6 3d^{10} 4s^2 4p^2$	-3881.0	E_3

positions. In extreme jj coupling the six equivalent $2p$ electrons are subdivided into two groups, one of two electrons with $j=\frac{1}{2}$, and one of four electrons with $j=\frac{3}{2}$. The vacancies in this case may be shown in terms of vacancies in these Stoner¹³ subgroups. Table IV shows how the positions of the extreme jj coupled levels may be estimated. The J values in column 2 of the table are those which would arise from the two equivalent, jj coupled, missing electrons, i.e., the $J=1, 2$ arising in the level whose energy is $L_{II}+L_{III}'$ are obtained from two equivalent p electrons one with $j=\frac{1}{2}$ and one with $j=\frac{3}{2}$. The primed symbols in column 3 of the table mean

$$L_I' = L_I + 72, \text{ etc.}$$

It is assumed that this 72 volt excess applies to all the primed levels. The calculated levels in column 4 of the table are obtained from Table I.

If the coupling were Russell-Saunders, the levels would be 3P , 1D and 1S arising from $2s^2 2p^4$, 1P and 3P from $2s^1 2p^5$, and 1S from $2s^0 2p^6$. Kennard and Ramberg¹¹ have pointed out that the equations of Goudsmit¹⁴ and Laporte and Inglis¹⁵ may be used to locate these levels in Russell-Saunders or any intermediate coupling. They have also computed the ratio of the exchange energy to the spin-orbit energy in these

¹³ E. C. Stoner, Phil. Mag. **48**, 718 (1924); also J. D. Main-Smith, *Chemistry and Atomic Structure* (D. Van Nostrand, New York, 1924).

¹⁴ S. Goudsmit, Phys. Rev. **35**, 1325 (1929).

¹⁵ O. Laporte and D. R. Inglis, Phys. Rev. **35**, 1337 (1930).

configurations in Na(11), Cl(17), K(19) and Cu(29). The coupling type for Ge(32) has been estimated by extrapolation of their results. Thus the coupling factor X , which they found to be 3.052 Rydberg units for $2s^1 2p^5$ and 0.505 for $2s^2 2p^4$ in Cu(29), is estimated to be 3.22 and 0.564 for the analogous levels in germanium.

If we consider the J values arising from $2s^1 2p^5$, we find that the $J=0$ and $J=2$ of the 3P are unique, that is, occur only once. Hence the total triplet width in the Russell-Saunders case is the width $(L_I+L_{II}')-(L_I+L_{III}')$ of the hypothetical jj coupled case. To the approximation in which we are working, this is merely the spin doublet separation of the singly ionized L shell. If we write the inverted triplet separations in the conventional form

$$\Gamma(J) = -\frac{1}{2}A\{J(J+1) - L(L+1) - S(S+1)\}$$

$\Gamma(J)$ represents the shift of a member of the triplet from the centroid of the triplet. From this equation we deduce that A , a convenient measure of the spin-orbit energy, is $1/3$ of the total triplet width, and that the centroid lies below the $J=0$ level of the triplet at a distance $2A$. From the values of Tables I and IV we then deduce the following. For the case in discussion A is 10.3 volts. The centroid of the triplet arising from $1s^2 2p^4$ lies at 2511 volts. The centroid of the triplet arising from $1s^1 2p^5$ lies at 2697 volts.

The separations of the levels from these centroid positions are given by the following expressions:

$$\begin{aligned} 2s^1 2p^5 \quad \Gamma(2) &= -A \\ \Gamma(1) &= A[(R+1)/2 \pm ((R-1)^2 + 8)^{1/2}] \\ \Gamma(0) &= 2A \\ 2s^2 2p^4 \quad \Gamma(1) &= A \\ \Gamma(0) &= A[1 + \frac{5}{2}R \pm \frac{1}{2}(25R^2 - 4(5R-9))]^{1/2} \\ \Gamma(2) &= A[R - \frac{1}{2} \pm \frac{1}{2}((2R-3)^2 + 16R)^{1/2}]. \end{aligned}$$

TABLE IV. Levels in germanium arising from doubly ionized L shells, assuming extreme jj coupling.

CONFIGURATION	J 's	ENERGY	VOLTS
$(2s^0)_{1/2} (2p^2)_{1/2} (2p^4)_{3/2}$	0	$L_I + L_I'$	2884
$(2s^1)_{1/2} (2p^1)_{1/2} (2p^4)_{3/2}$	0, 1	$L_I + L_{II}'$	2718
$(2s^1)_{1/2} (2p^2)_{1/2} (2p^3)_{3/2}$	1, 2	$L_I + L_{III}'$	2687
$(2s^2)_{1/2} (2p^0)_{1/2} (2p^4)_{3/2}$	0	$L_{II} + L_{II}'$	2552
$(2s^2)_{1/2} (2p^1)_{1/2} (2p^3)_{3/2}$	1, 2	$L_{II} + L_{III}'$	2521
$(2s^2)_{1/2} (2p^2)_{1/2} (2p^2)_{3/2}$	0, 2	$L_{III} + L_{III}'$	2490

In these expressions $R=X/A$. The A for germanium is 0.757 Rydberg units, hence the R 's are 4.25 and 0.745. The results are shown in Table V. The Auger electron energies of column 4 of this table are obtained by subtracting the values of column (3) from 11,066, which is the energy of the K state in volts.

The positions of the lines computed in Table V are indicated in Fig. 2 which shows the experimental curve. It is seen that the calculated lines fall well within the region of the experimental curve.

RELATIVE INTENSITIES IN THE L^2 GROUP

The relative intensities of the Auger electron beams ejected from the L shell have been theoretically investigated by Burhop,¹⁶ Massey and Burhop,¹⁷ and Pincherle.¹⁸ The computations of Massey and Burhop take into account the relativistic wave functions which are important for heavy elements. The calculations of Burhop and of Pincherle may be compared, since they are both nonrelativistic. Their results are as follows:

	$2s^02p^6$	$2s^12p^5$	$2s^22p^4$
Burhop	15	51	100
Pincherle	10	36	100

The headings of the columns are the final atomic states after the ejection of an Auger electron. It is seen that the theoretical predictions do not agree to better than 30 percent.

Any attempt to test these predictions from the experimental curve involves resolving it into component curves. In view of the small energy differences between the L^2 levels and the asymmetry of the electron line due to the geometry of the spectrometer¹⁹ and the straggling of the electrons on the low velocity end of the spectrum, an unambiguous resolution into components was not possible with the present resolving power of the apparatus. However, one can effect a reasonable resolution by studying the low velocity side of the spectrum of the K photoelectrons of

TABLE V. Estimated energies of L^2 levels and corresponding Auger electrons in germanium.

CONFIGURATION	LEVEL	ENERGY	AUGER ELECTRON ENERGY
$2s^02p^6$	$1S_0$	2884 volts	8182 volts
$2s^12p^5$	$1P_1$	2746	8320
	$3P_0$	2718	8348
	$3P_1$	2702	8364
	$3P_2$	2687	8379
$2s^22p^4$	$1S_0$	2571	8495
	$1D_2$	2543	8523
	$3P_1$	2521	8545
	$3P_0$	2512	8554
	$3P_2$	2494	8572

germanium ejected by the silver $K\alpha_{12}$ lines and arrive at an estimate of the shape of the various groups. The dotted curves of Fig. 2 are such an estimate. The ratios of the areas under the three curves are 100 : 26 : 26. Due to the lack of uniqueness in the treatment of the unresolved experimental curve it is doubtful if much confidence can be placed in these ratios. In order to study in more detail these lines, a new spectrograph of higher resolving power is being built.

RELATIVE INTENSITIES OF THE L^2 AND LM BANDS

In the work of Pincherle previously mentioned, the relative probabilities of $K \rightarrow L^2$ and $K \rightarrow LM$ transitions is computed, a value of 100 : 58 being obtained. This ratio should be given quite accurately by the experimental curves of Fig. 2. The ratio of the areas under the two curves is 100 : 31. The hump on the low velocity edge of the LM band was not included in this area because it was impossible to correlate it with any $K \rightarrow LM$ transition. If, however, it is included, the above experimental ratio becomes 100 : 34. Any possible correction for differences in scattering and absorption of the electrons would tend to increase the discrepancy between theory and experiment. It should be noted that in view of the extraordinary thinness of the germanium film any difference in absorption between the L^2 and LM electrons would be negligible.

In conclusion, the author wishes to express his appreciation to Professor S. K. Allison who suggested this problem and gave valuable advice during its completion.

¹⁶ E. H. S. Burhop, Proc. Roy. Soc. Lond. **A148**, 272 (1935).

¹⁷ H. S. W. Massey and E. H. S. Burhop, Proc. Roy. Soc. Lond. **A153**, 661 (1936).

¹⁸ L. Pincherle, Nuovo Cimento **12**, 81 (1935).

¹⁹ W. A. Wooster, Proc. Roy. Soc. Lond. **A114**, 729 (1927).

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